MASTERBATCHING TECHNIQUES

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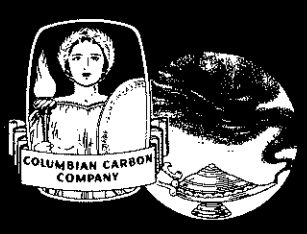

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See fig. 5

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Synopsis

MASTERBATCHING TECHNIQUES

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"Masterbatch" is a rubber industry term that denotes a concentrated predispersion of some compounding ingredient in rubber intended as a "stock" item for later use in a complete formulation. The plastics industry is adopting the same terminology just as it has adopted and adapted much rubber processing equipment and techniques. Such premixes (masterbatches) have long been commercially available in many media under the name of predispersions or base dispersions.

A variety of masterbatch techniques adapted to the nature of the plastic, resin, or elastomer, and to the end use, have been developed. With pigments generally, and carbon black particularly, the commonest procedure has been to mill at high or even extreme viscosity. This brings high shearing forces into play to effect dispersion. Significant variations of this basic method are made to attain specific objectives.

The general approach for carbon black-rubber masterbatches has been high viscosity milling. The approach through latex is the oldest technique and the one most persistently pursued. Prior to the development of the synthetic rubber industry in the U.S.A. during World War II latex masterbatching was economically unattractive. When rubber latex and carbon black became available in the same country interest in latex masterbatching revived to be further stimulated by the increase in capacity of installed rubber processing equipment this technique made possible. In 1952 production of latex-black masterbatch reached a peak of 132 thousand long tons. Competition, traditional in the rubber industry, called for a better process and a better black-rubber masterbatch. The Columbian system represents a step in this direction. It is continuous and simple in theory and operation. More important, it produces significant improvements in tire tread wear and shortens processing time in the tire factory. In essence, it brings the two components, rubber and carbon black, together as colloids with minimum physical and chemical interference with their ultimate union.

MASTERBATCHING TECHNIQUES

By

H. A. Braendle

Introduction

Many parallels exist between the rubber and plastics industries. I quote three only.

1. Early Enthusiasms and Disappointments. When rubber was first brought out of the Amazon jungles it inspired many by its potentials. Much capital was ventured and lost during the early history of the rubber industry. The stories of Charles Goodyear and Thomas Hancock and their persistence in the face of failures are supreme examples of faith. Early ventures in the exploitation of plastics were equally disheartening. The early plastic toys and novelties were too fragile and brittle, and put the whole plastics industry into disrepute.

2. Steps Ahead. Goodyear discovered vulcanization, eliminating the thermal degradation of raw rubber. In turn modern chemists have built better and tougher plastics. Toys are now made of polyethylene which the average moppet can enjoy for quite a while.

3. Reinforcement. Pure gum or lightly compounded vulcanized rubber started the rubber industry ahead on a sound basis. In due course, however, the reinforcing effect of additives, particularly carbon black (1), made possible the development and growth of the automotive industry.

The newer plastics, particularly the thermoplastics, so marvelous in their pure or lightly compounded state, have stimulated research into the potentialities of reinforcement. I believe it can be safely said that in the one area of carbon reinforcement alone, and profiting from the experience of the rubber industry in masterbatching techniques, the plastics industry can look forward to expansion and diversification into areas currently not even contemplated.

Rubber Masterbatches

The term "masterbatch" until quite recently has been peculiar to the rubber industry. One early glossary (2) gives these definitions:

1. A batch of uncured rubber containing a high percentage of but one pigment.

2. A batch containing a much higher concentration of one special pigment than is usual in the regular mix.

These fit very nicely masterbatches of, say: sulfur, accelerator, antioxidant, zinc oxide or the like which are used in relatively small proportions in the final mix. Here masterbatching gives greater accuracy of proportioning or better dispersion. This was probably the original meaning but in actual practice this has been considerably broadened, particularly where such reinforcing pigments as carbon black are concerned.

Possibly a better definition would be: A predispersion or mix of one or more ingredients in a base polymer which may later be combined with other ingredients or even other masterbatches to make a variety of products. So defined, the term fits the etymology of the

expression in that it carries the connotation of master or chief batch on which others depend or from which others are made.

Practically every ingredient listed in the compounder's book has been prepared in masterbatch form to get better dispersion; e.g., zinc oxide or carbon black; to permit more accurate proportioning; e.g., accelerators, antioxidants and other materials used in relatively small amounts and insoluble sulfur (which must be mixed cold and added as the final ingredient to stocks which are stored for extended periods in the raw state and which must be non-blooming at the time of use and cure). More recently, sizable proportions of oil have been premixed with high molecular weight synthetic rubber for economy and convenience. These latter are also masterbatches even though they are frequently referred to as oil-extended polymers and considered as all polymer in later formulation. But the masterbatches produced in largest volume are undoubtedly those with carbon black alone or with some emollient. When one recalls that in the total of all rubber goods manufactured, the total ratio of carbon to natural rubber is 25% and the total ratio of carbon to SBR type rubber is 45%, the importance of black masterbatching techniques is understandable. In the present discussion we shall therefore pretty well confine ourselves to carbon black since most of the principles discussed will apply to other pigments as well.

In the early 1920's the present author, working under the direction of W. B. Wiegand, developed a series of products of unusually

high black loading. In addition to shoe solings of excellent wear, all-rubber footwear and all-rubber tires were developed (3, 4). Claim 3 of Canadian Patent No. 250,918 to W. B. Wiegand reads:

> "An article of footwear including sole and upper portion and consisting essentially of rubber compound containing as an essential ingredient between fifty (50) parts and one hundred (100) parts by weight of finely divided carbon black to each one hundred (100) parts by weight of crude rubber in the compound."

Claim 2 of Canadian Patent No. 274,299 to W. B. Wiegand reads:

> "An all rubber tire manufactured as set forth in claim 1, consisting of a casing and an inflatable inner tube, the casing composed of rubber composition containing as essential ingredients between 60 and 120 parts by weight of carbon or lamp black to each 100 parts of crude rubber in the composition."

These stocks taxed the best mixing equipment then known and it was not uncommon to allow five of the mills on a six-mill line to run idle while a mix was prepared on the sixth in order to concentrate enough power on that one mill. Another expedient used was to add a solvent such as toluene or xylene to the mix to act as a disappearing emollient during the incorporation of the carbon black. An outstanding effect was the extreme smoothness and shininess of the cut surface of the stock, then as now an excellent criterion of overall good black dispersion. From this beginning it was an easy step to the premixing of carbon black into rubber at higher-than-end-use concentrations to get improved dispersion. Frequently it was found advisable to add the diluting rubber in small increments to the freshly made masterbatch on the mill while it was still

warm and plastic. Like many developments in any field of technology, this approach was followed by so many investigators that no one knows who first called this the masterbatch method. It was so described in trade bulletins as early as 1931 (5).

A typical masterbatch comprised:

Hevea	100
Channel black	60-75
Pine tar	3-4

The exact proportions were a compromise based on equipment available, cost, and a balance between improved quality by better black dispersion and lowered quality by oxidation of the Hevea.

In some places the term "masterbatch" was loosely applied to the premix of carbon black in rubber for tire tread compounds in which the black to rubber ratio was no higher than for the final compound. Some factories, for the sake of good dispersion, put a master of Hevea, black and some oil into the Banbury for a series of short runs with intermediate rest periods to permit the natural polymer to regain its nerve. Others put together the rubber and black master at high temperature and high speed in the Banbury, and withheld some of the ingredients because of danger of chemical breakdown. In still other shops these high temperatures and high speeds resulted from economic necessity and the shortening of overall processing time, and some of the more heat sensitive materials had to be withheld for later incorporation.

It is, of course, impossible to detail all of the variations of the rubber-carbon masterbatch techniques which have been used. Based on equipment and the personal preference of the compounder and mill room supervisor, practically every gum shop had its own preferred method. Some techniques, however, will be described because of the unique results obtained. In 1941 Bradley (6) was granted a patent on a masterbatch technique for preparing natural rubber-carbon black treads in which he prepared a black master of around 60% of carbon on the rubber and subsequently reduced it to final tread ratio by addition of diluting rubber. He, however, introduced an intermediate step, namely, static heating of his masterbatch prior to finishing. Figure 1 illustrates his preferred result, namely, a dispersion of highly pigmented, very tough rubber in a matrix of unpigmented or, at best, lighly carbon reinforced diluting rubber, in a sense a two-phase system. This did give improved wear and improved resilience as claimed but it did not receive extended application, possibly because of the cost of the extra steps.

In March 1949 (7) Columbian Laboratories first announced the carbon gel concept with GR-S type polymer which was later (8) discussed in greater detail. In April 1950 (9) Braendle, Estelow and Wiegand discussed the application of the carbon gel principle to natural rubber reinforcement. Masterbatches of smoked sheets and carbon were made at 75 to 80% of VFF on the rubber with some pine tar, and mixed at high

FIGURE 1

temperature (375-380°F.). Both modulus and tensile strength were enhanced over a standard control mix. It was found preferable to dilute the masterbatch while it was still relatively soft and warm and then finish the stocks in a slow-speed Banbury at normal processing temperatures, namely, below 300°F. Tire treads so prepared outwore the then best cold rubber treads by a margin of 5%. There were indications that when the masterbatches were rested for 24 hours or longer before dilution, a condition similar to that described by Bradley resulted, namely, a failure of the diluting rubber to penetrate the carbon gel complex produced by hot milling with high concentrations of carbon in smoked sheets.

Because of the higher cost of Hevea over synthetic very little was done in the U.S.A. on this method of masterbatching for tire treads but on the Continent, where synthetic was not as readily available, at least one rubber company confirmed this effect.

During World War II, as soon as the American synthetic rubber industry got under way, interest in latex masterbatching of carbon black in synthetic rubber latex was quickly revived as a means of extending mixing capacity in the tire factories (10). Early work in Europe during the period 1924-29 was reviewed and a 1935 U.S. Patent (11) to Beck and Mueller-Conradi was used as the starting point for the latex black masterbatching process developed in the U.S. Government synthetic rubber program. This process, as is well known and as described by

Beck and Mueller-Conradi, prepares a slurry of black with some surface active or dispersing agent, adjusts the pH of slurry to match that of the latex, blends the two as thoroughly as practical and then precipitates or coagulates the two together. This was an important part of the U.S. Government synthetic rubber program and production reached a peak of 132,000 L.T./a. Under full scale commercial operation, expectations of those who developed the process were not quite met. Furthermore, the full implications of the carbon gel concept in synthetic rubber processing and the necessity of setting minimum as well as maximum Banbury dump temperatures, made possible better wearing dry mixed treads of much more uniform quality than previously possible. This and other advances in mixing technology left synthetic rubber latex-black masterbatch with a net loss of something of the order of 5-10% in road wear compared with dry mixes. As a result, consumption of synthetic black rubber-black masterbatch fell off and some synthetic plants even closed down their black masterbatch operations. But, the latex masterbatching approach had enough inherent advantages over dry mixing to warrant further investigation. On May 15th, 1957 (12) the present author had the privilege of describing an improved method of masterbatching synthetic rubber latex and carbon black before the Joint Conference A.C.S. - C.I.C., Divisions of Rubber Chemistry, Montreal, Canada. The Columbian process described in the above-mentioned paper has a number of advantages over earlier methods:

1. No dispersing agent is used with the carbon black and there is no blocking off of the active sites on the surface of the carbon particles to interfere with their natural affinity for the rubber molecule.

2. The process is continuous and, by securing substantially instantaneous, intimate and uniform admixture of the latex and black slurries, gives a higher degree of uniformity of distribution of black in the finished masterbatch. We come closer to the theoretical picture presented by Adams and Howland (10) in their Figure 1 reproduced here as Figure 2.

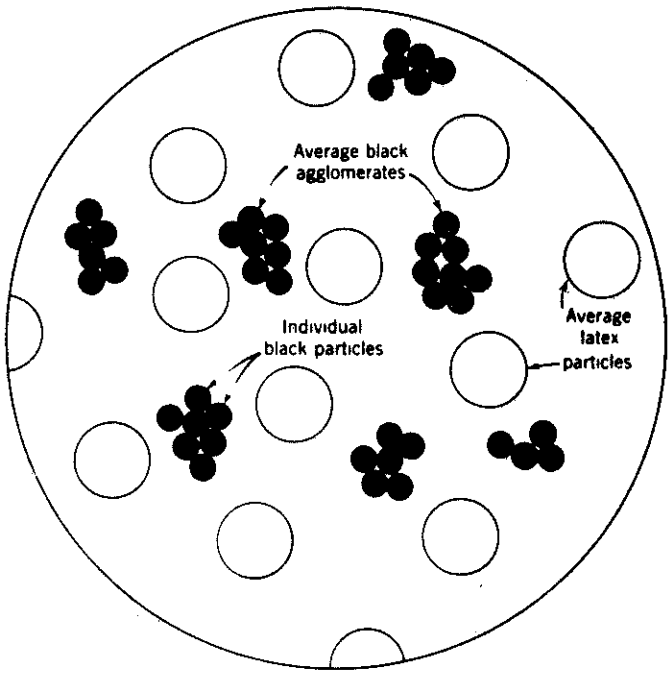
3. With standard cold rubber latex, the major part of the softening agent or oils of the final tread compound can with advantage and facility be added to the masterbatch.

4. The process works equally well with high molecular weight latex and extending oils (25%, 37.5% or even higher on the base polymer) along with the black.

5. The unstabilized black slurry or the normal affinity between rubber and carbon black, depending on one's point of view, causes the carbon black to act as the creaming agent for the latex, a step desirable in coagulation to get a porous, washable crumb.

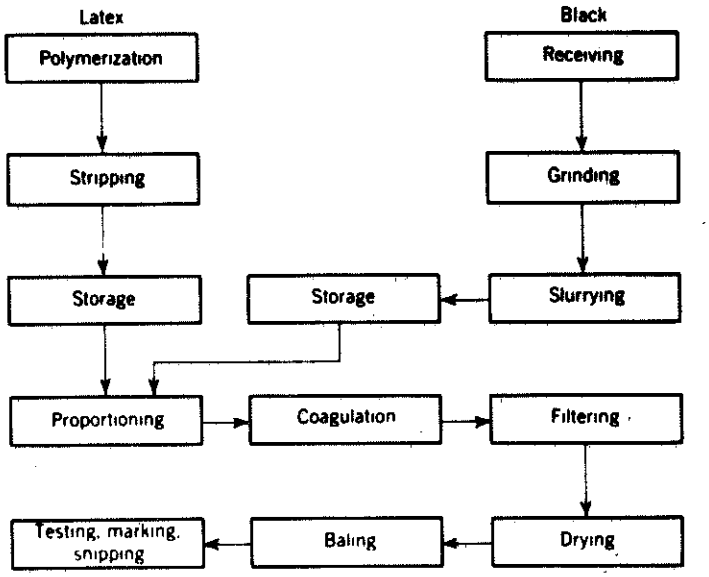
6. Great latitude in composition of the final masterbatch (percentage of black and percentage of oil) is entirely feasible.

Figure 3 taken from the Adams and Howland paper (10) shows the sequence of operations in the conventional black rubber system as



Theoretical Particle-Size Relation—GR-S Latex and EPC Black

FIGURE 2



Latex Masterbatching Process—Condensed Over-All Flow Diagram

FIGURE 3

developed under Government operation. While the diagram may not have been designed to do so, it does illustrate batch operation with the necessary large slurry, holding, and blending tanks. One of the major problems was the retention of the slurry in proper dispersion and fluidity, a difficulty that prompted our search for a better and simpler process.

Figure 4 is a flow diagram of the Columbian process. This, as has been explained above, is streamlined and continuous with no hold-over anywhere along the line from the delivery of the black, the latex and the oil to the preparation and coagulation area.

In its simplest terms the process consists of these parts: The carbon black is stirred into water alone with extreme vigor to break up the carbon black beads, the carbon particle agglomerates within the beads to give a reasonable approximation to particulate dispersion. The black is kept suspended not by colloidal action but by continuous vigorous agitation, and the latex is blended with it under maintained violent agitation and said blend is dropped into an acid coagulating tank. Oil, either with or without emulsification, is similarly added with violent agitation during the process of blending these two separate streams and is co-precipitated with the rubber and black. Again we attain a better than average distribution of the oil droplets in the rubber coagulum. In Figure 5 is shown some of the detail of the construction of the machine devised to produce these black slurries (13). This is simply a high-speed

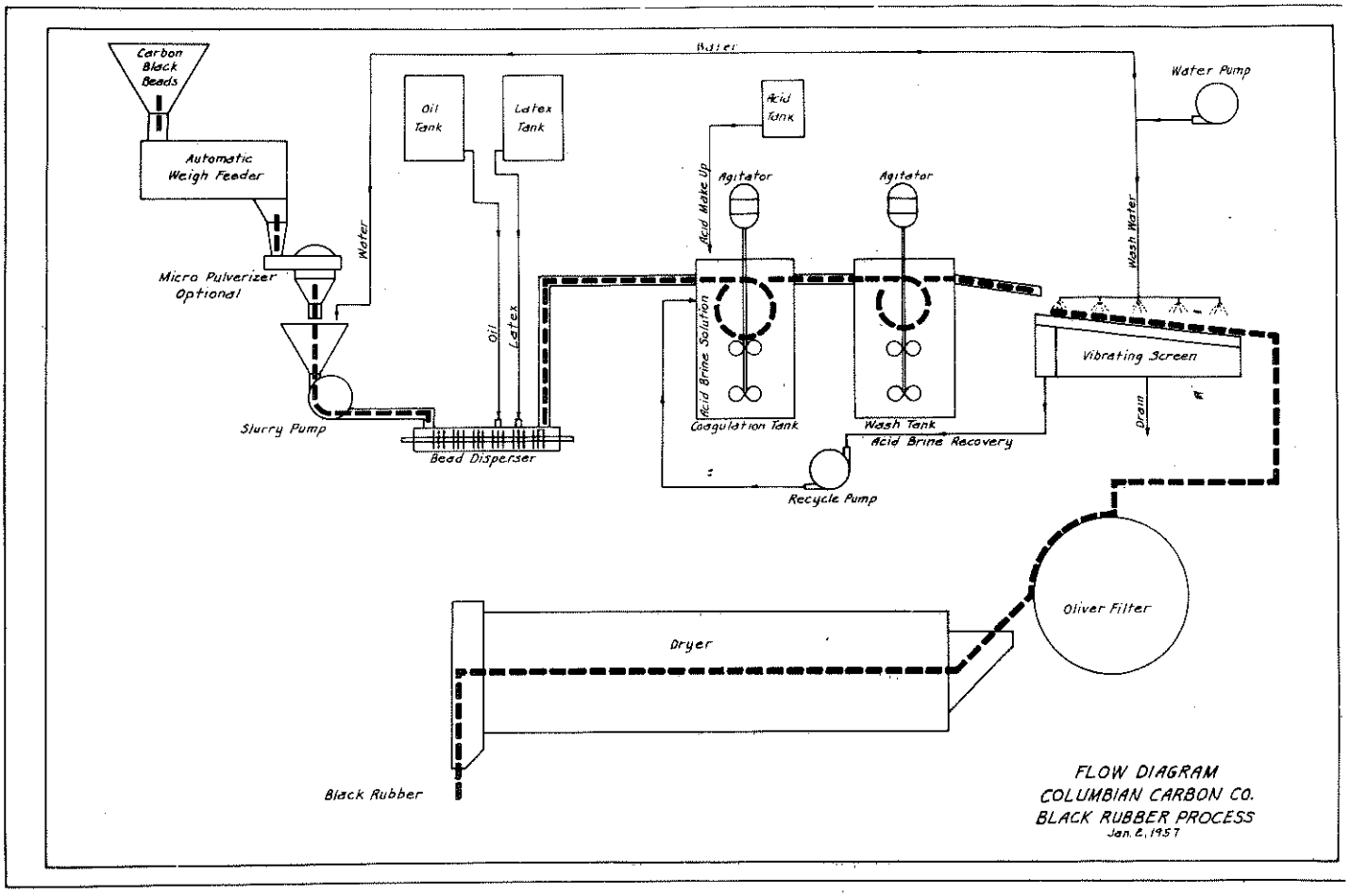


FIGURE 4

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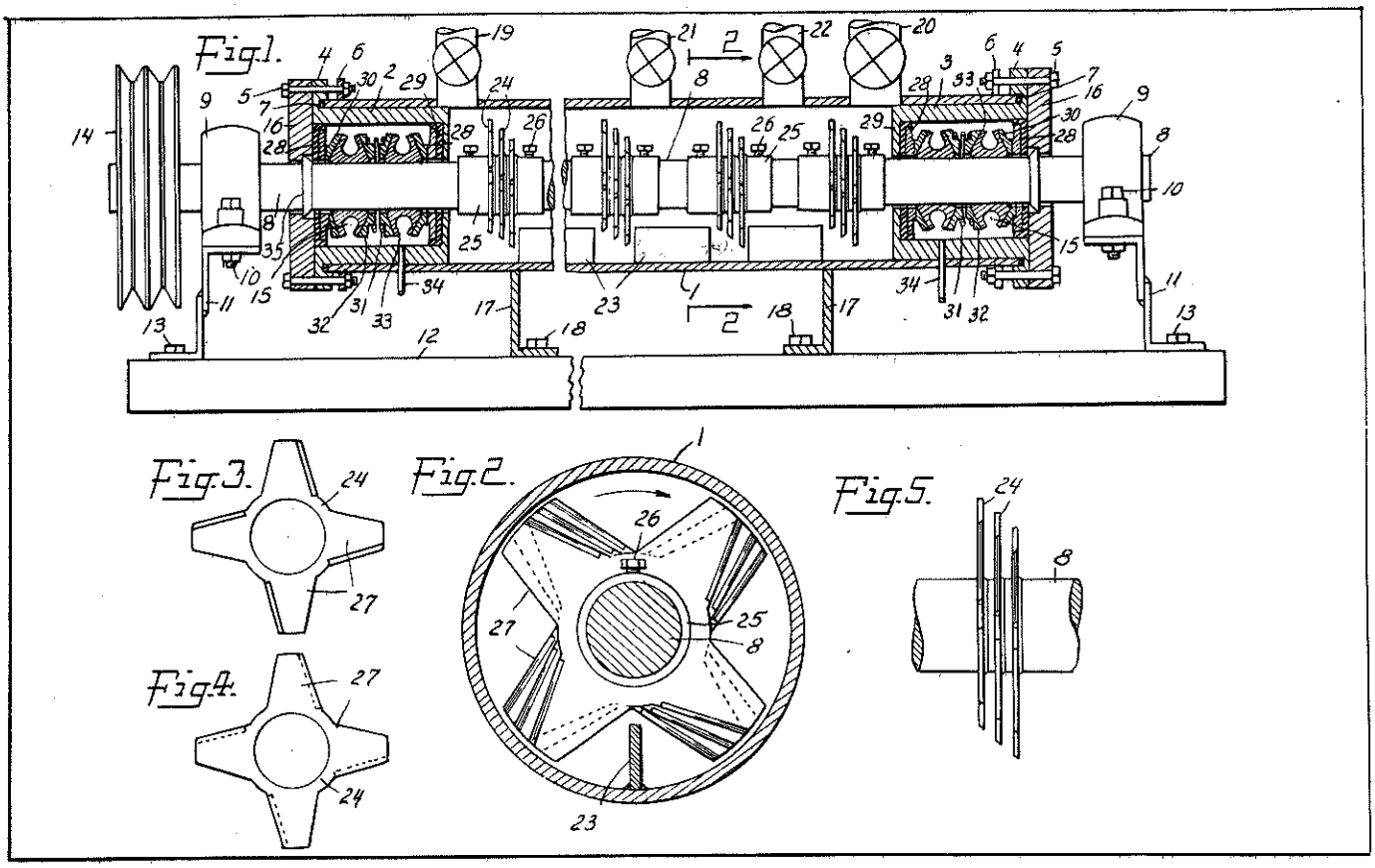

FIGURE 5

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stirring device in which the carbon black is dispersed, not ground, into water by high hydraulic impact and shear. This elimination of grinding has been an important factor in the commercial success of the process. In Figure 6 is shown a photograph of one of these units. The motor normally is mounted on the inlet end and runs at 3500 to 6000 RPM, depending on the type of black and the throughput desired. The latex may be introduced into the machine itself or may be blended with the slurry stream in any sort of high velocity jet stream mixing device. Figure 7 shows the rotor of this dispersing machine. While not discernible on the photograph here, the little rotor blades in groups of three have sharpened edges both leading and trailing. Any propellor action of one set of blades is neutralized by the reverse pitch on the next set. To prevent the entire mix from rotating as a solid core through the machine (avoiding shearing action), stators are welded to the inside of the barrel of the machine between successive sets of rotor blades. These can be seen in Figure 8, a photograph of the interior of the barrel of the machine. This dispersing machine is naturally not the only means by which satisfactory dispersion can be produced but it does have some unique features which make it work better than its predecessors or than its simplicity would indicate. Black rubber prepared by the Columbian method, as repeatedly shown in actual road tests, wears 15 or more per cent better than identically compounded Banbury mixes of dry ingredients. Treads made from Columbian type black rubber also have

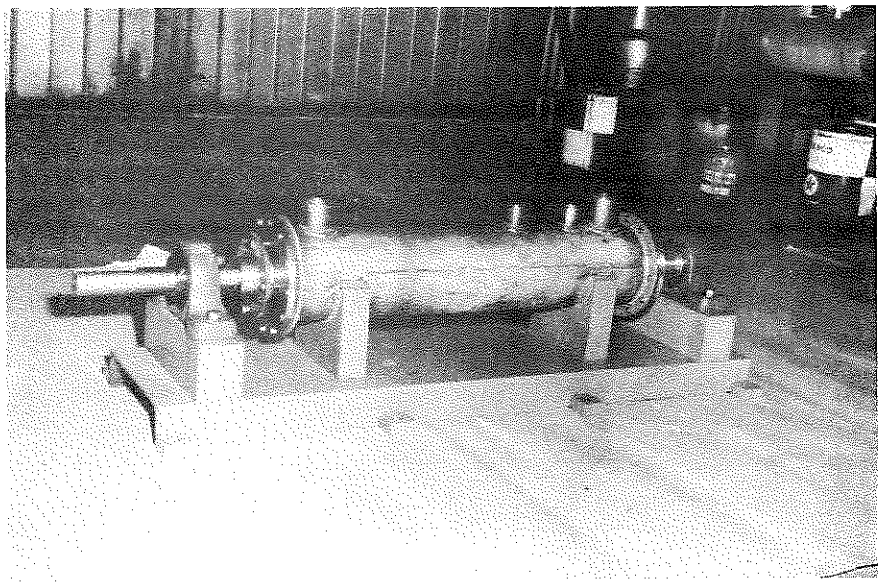


FIGURE 6

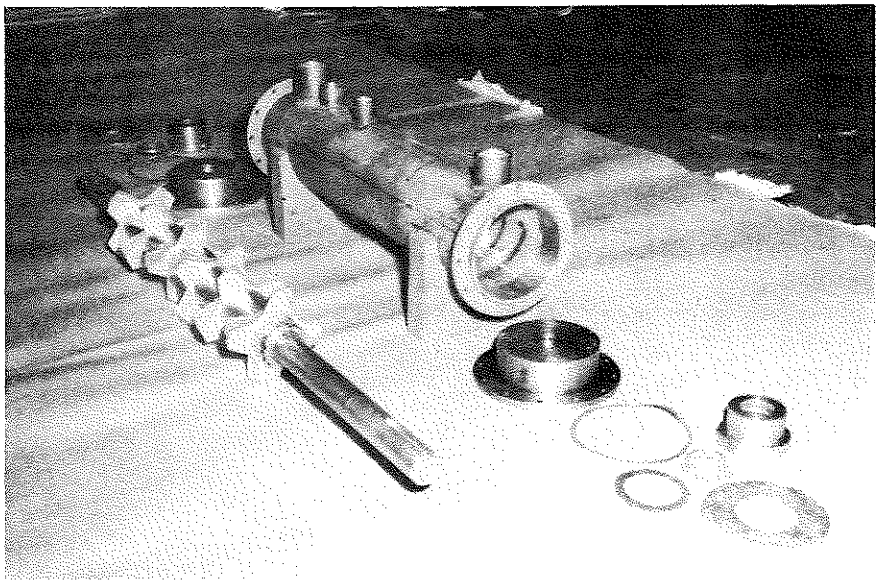


FIGURE 7

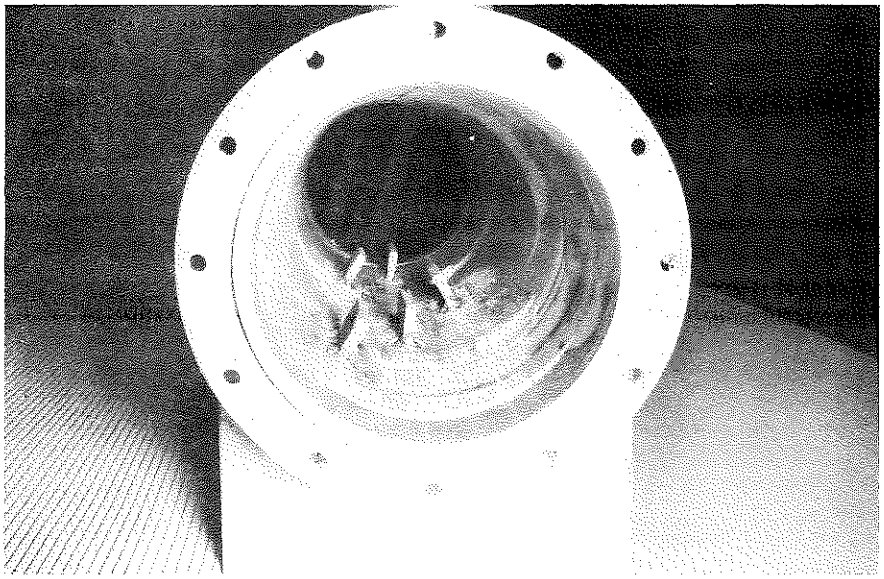


FIGURE 8

lower Mooney viscosity, much better dispersion of black in the rubber and better hysteresis in the final vulcanizate than their dry mixed counterparts.

Another evidence of the better dispersion or, more properly, distribution of carbon and polymer in the masterbatch is the non-crocking or cleanliness of the finished bale. This represents a considerable economy in that bales can be stacked and shipped merely with normal dusting and without wrapping.

Mention has been made of the carbon gel concept in tire tread compounding and processing. Where dry mixing, as in the Banbury, is employed this calls for careful control of maximum and minimum dump temperatures as pointed out before. Excessive Banbury dump temperatures, while giving enhanced road wear, also result in bad tread cracking. Figure 9 shows an electron micrograph of a microtomed section of a cured tread stock in which dump temperature was deliberately above desirable limits. Note the aggregation of the carbon black in dense areas with clear areas of unpigmented rubber in between. Note also the resemblance between this picture and the micrograph of the preferred Bradley (Fig. 1) tread. Here in LTP we have a micro repetition of the pattern developed by Bradley on a larger scale. There is, however, one very important difference. Bradley used natural rubber with good pure gum strength. LTP without carbon black is of course notoriously weak, hence the bad

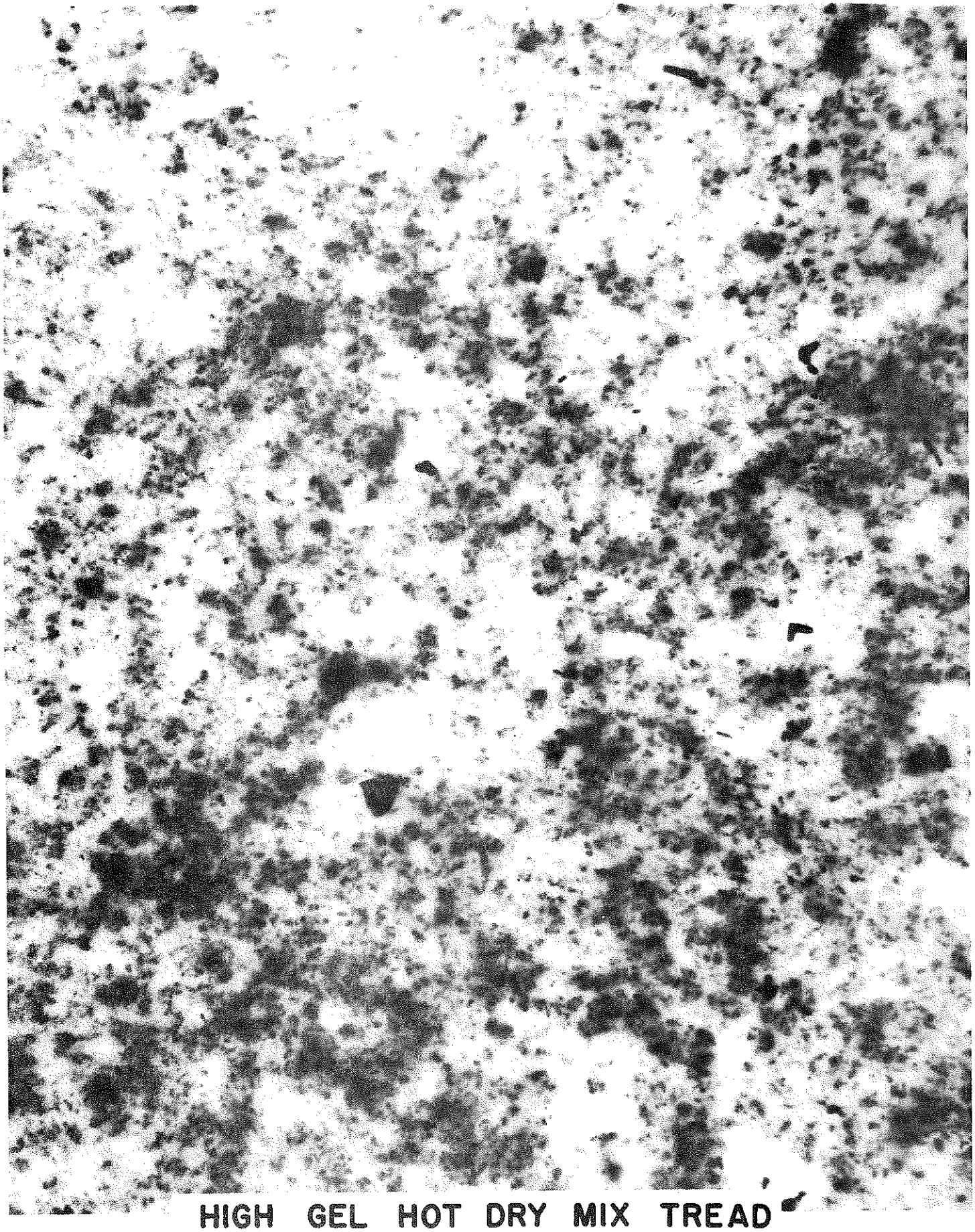


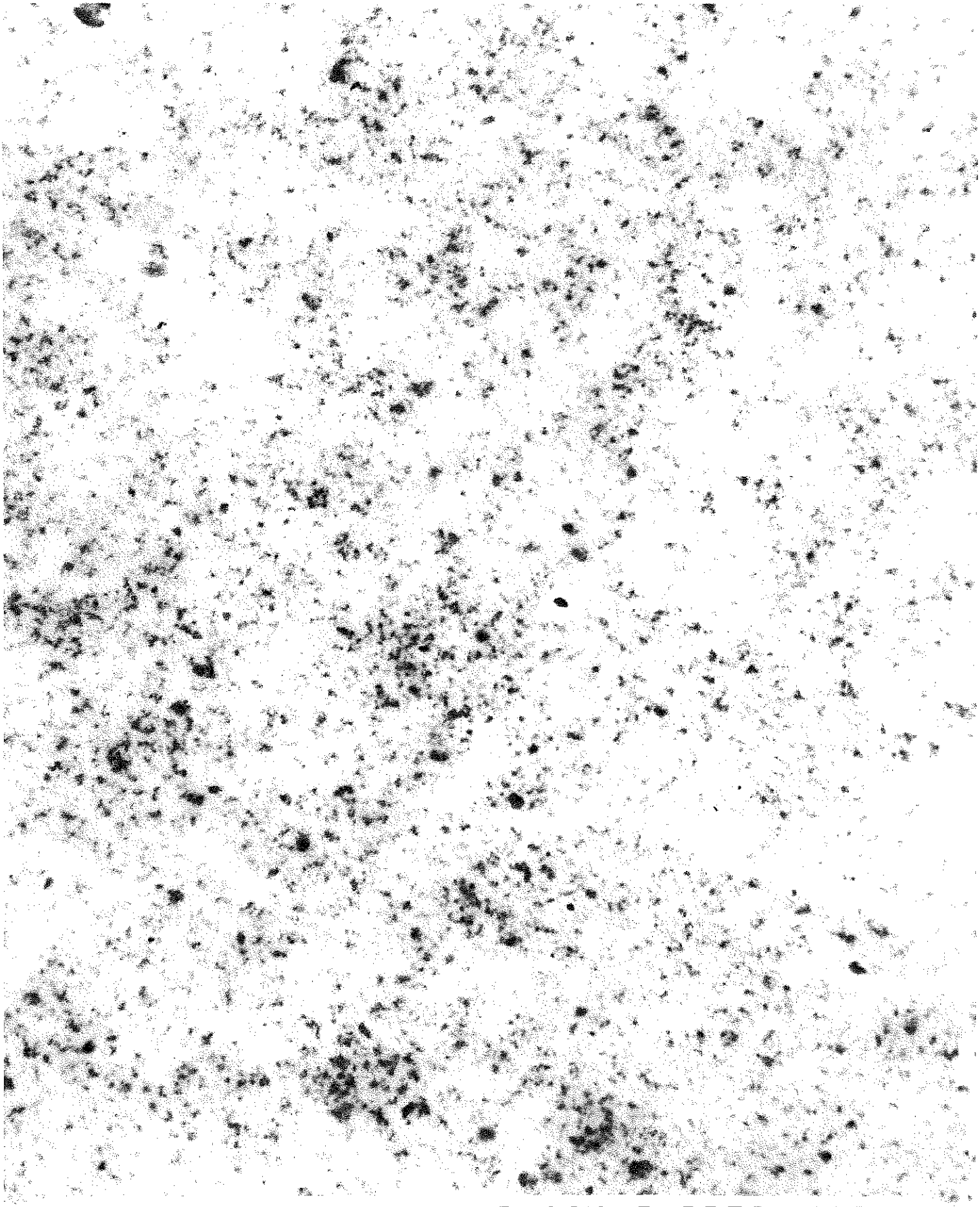
FIGURE 9

cracking performance of a GR-S type tread in which excessive heating causes a separation of the carbon gel complex and the sol rubber. In Figure 10 we show an electron micrograph of a similarly microtomed section of a tire tread made from Columbian type black rubber. Note particularly the uniform distribution of the carbon gel in small units and the relative absence of large areas of unreinforced polymer. We believe that, in addition to the elimination of the interference of dispersing agents with the formation of rubber-to-carbon bond, we now have a means of developing adequate carbon gel for reinforcement with excellent distribution and therefore uniform reinforcement of the whole tire tread (to minimize tread cracking). This therefore represents visual proof of the title given to the paper presented in Montreal (12), namely, "Improving the Carbon-Rubber Bond." It is improved quality-wise through the elimination of dispersing agents and the blocking off of active sites on the carbon and by a better and more effective distribution of the final carbon gel in the finished tread.

Plastics Masterbatches

As mentioned above, the term "masterbatch" has until recently been peculiar to the language of the rubber technologist. It occasionally occurs in the literature of plastics, at times in quote marks indicating the newness of its use.

The excellent properties of modern plastics compared with celluloid and other early plastics were at one time quite sufficient to



COLUMBIAN PROCESS BLACK RUBBER TREAD

FIGURE 10

spur their commercial exploitation, and for a long period the addition of anything but colorants was of no interest. In this sense the plastics industry is following the course of the rubber industry. The great expansion of the rubber industry came with the discovery (1912) of the unique reinforcing power of carbon black giving improved wear to automobile tires just then appearing.

One of the properties of modern plastics deliberately developed is clarity or water whiteness making possible the manufacture of brightly colored products of quality and permanence. The new plastics are so good and so stable in their properties that for many uses they need no improvement. The combination of glass fibers and polyester resins was possibly the opening wedge to the reinforcement of plastics. A great variety of materials can be added to the thermosetting resins as colorants and extenders without lowering the physical properties of the base resins below the requirements of the finished article.

As the range of applications of plastics was extended, special effects were needed and in some instances shortcomings developed. Polyethylene wire insulation for outdoor use needed protection from U. V. It didn't take much imagination to find that carbon black here, as in protective coatings, formed a good barrier to U. V. and its destructive action. For maximum effectiveness the carbon black is generally prepared in a masterbatch and subsequently fluxed into the final compound. This gives effective dispersion and maximum protection.

Actually, masterbatches of carbon black in synthetic resins and thermoplastics have been in commerical production for many years under various trade names and classified as colloidal dispersions or base dispersions. Originally developed for the protective coatings industry, it was a logical step to modify them for solid or extrudable plastics. These include bases such as:

Nitrocellulose
Vinyls
Varnish resins of various sorts
Ethyl cellulose
Chlorinated paraffins
Styrene
Cellulose acetate
Polyethylene

For use in protective coating, the concentration of black in the masterbatch is generally lower than for use in a thermoplastic molding or extrusion. The latter, because of higher black concentration, becomes insoluble just as the higher proportions of carbon in rubber are insoluble (8). (See Figure 11.) Here Sweitzer et al, in discussing bound rubber vs. carbon concentration in the masterbatch, state:

> "These loading tests would indicate that the continuity of the carbon-rubber system throughout the masterbatch, which is responsible for its non-dispersability, is broken as loading is decreased, obviously not due to a variation in the carbon adsorption effects which should remain constant regardless of the loading, but rather to a break in the linkage between the individual carbon-rubber units. That this linkage involves rubber rather than carbon is suggested by the drop in bound rubber values at the lower loadings."

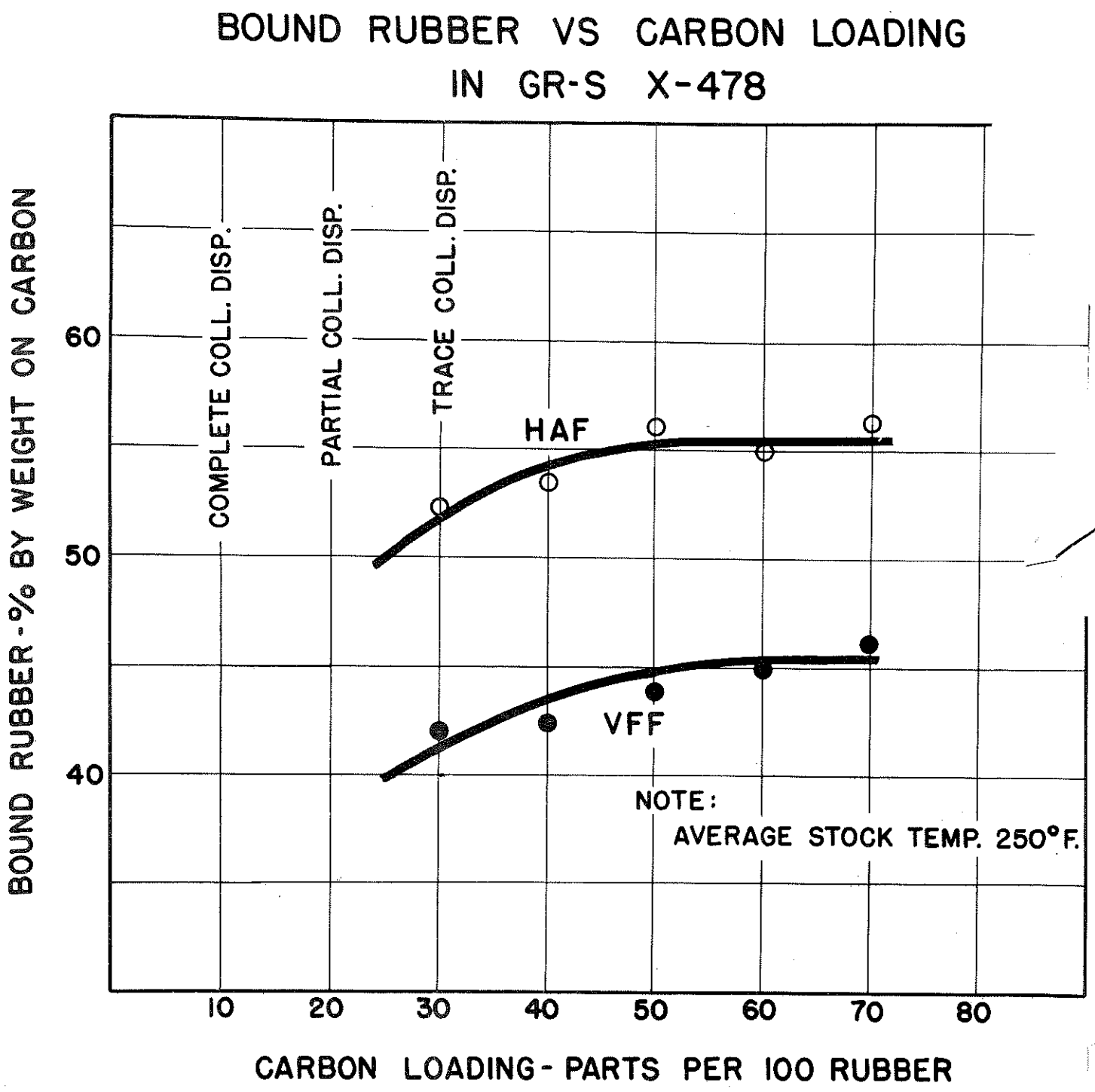

BOUND RUBBER VS CARBON LOADING
IN GR-S X-478
BOUND RUBBER - % BY WEIGHT ON CARBON
60
50
40
COMPLETE COLL. DISP.
PARTIAL COLL. DISP.
TRACE COLL. DISP.
HAF
VFF
NOTE:
AVERAGE STOCK TEMP. 250°F.
10
20
30
40
50
60
70
80
CARBON LOADING - PARTS PER 100 RUBBER

FIGURE 11

The analogy between the two seems obvious: there is some form of bond between carbon black and polymer; and, when enough carbon black is added to reduce the proportion of free polymer to some as yet undetermined critical level, the polymer-carbon lattice becomes coextensive with the masterbatch and solubility decreases or even stops.

The practical limits set in commercial masterbatches are:

1. for solution work, the highest loading which will give solubility and maintained dispersion of the carbon black on dilution; and

2. for solid plastics work, the maximum black loading which on fluxing into more of the same or some other thermoplastic will still maintain at least an approximation to particulate dispersion.

The common denominator of all these masterbatches is that they are prepared by high viscosity milling of a high loading of black on the base polymer in order to generate the necessary shearing action to separate and disperse the black in the base. Various dispersing agents are used depending on the polymer, the commonest being metallic soaps (U.S. Patents 1,987,980 and 2,173,445) and polyamines. Plasticizing agents are quite commonly added both for improving the processing of the black master and for speeding up solution or fluxing into the final composition. Here again, the parallelism with rubber is noted.

The nature of the carbon-to-polymer bond still baffles us and it is too early to do more than speculate. In some cases at least, oxygen is probably involved. Thus it has been found in making carbon

black-resin masterbatches for air drying enamels that the reduction of the high viscosity milled masterbatch must be started at once lest complete insolubility set in. This is generally done in an internal mixer of the Banbury or Z-blade type with the solvent added slowly and in small increments to prevent the masterbatch from breaking up into lumps to float in the more dilute portions. Dilution to final concentration does not have to be carried out at once but may be stopped at a paste consistency carrying 15 to 20% of carbon. (Fig. 12) Here we again see a parallel with rubber where carbon gel increases with resting (8) after dispersion of the black via milling.

Up to the present, carbon black-plastic masterbatches have been used primarily to get a good predispersion of the carbon black for blackness or U. V. light shielding where the final concentration of carbon in the vehicle is of the order of 3%. This applies to both solution and to molding and extrusion where the masterbatch is fluxed into the diluting polymer by hot milling of some sort.

In most instances the fabricators of enamels or plastic articles have found it more economical to buy masterbatches at high black concentrations from specialists in the field. This saves investment in equipment and takes advantage of years of know-how developed by these specialists. Recently reports are heard of the successful reinforcement of such materials as polyethylene with large volumes of carbon black. In one case at least, an unidentified cross-linking agent is mentioned.

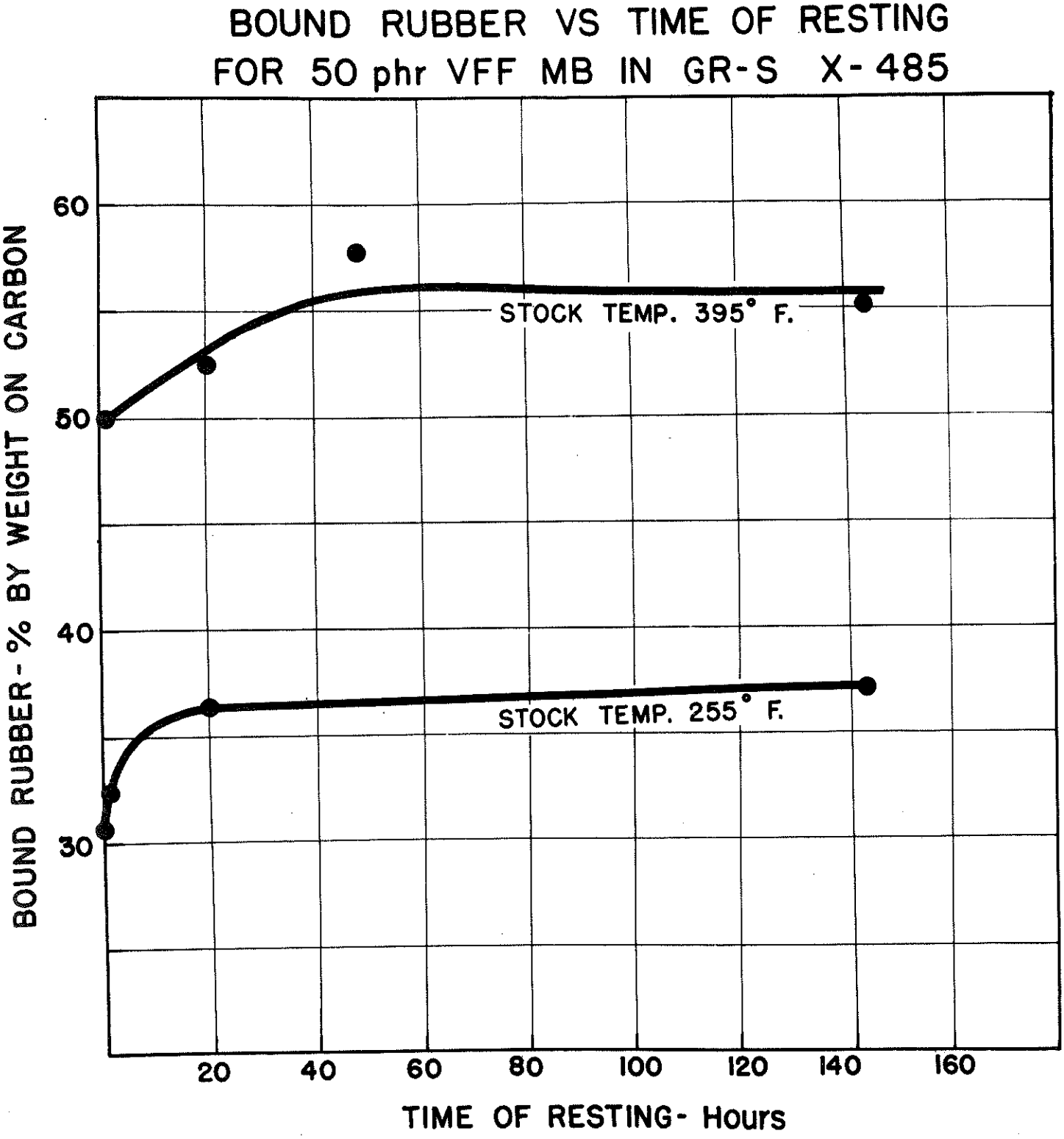

BOUND RUBBER VS TIME OF RESTING
FOR 50 phr VFF MB IN GR-S X-485
BOUND RUBBER - % BY WEIGHT ON CARBON
60
50
40
30
STOCK TEMP. 395° F.
STOCK TEMP. 255° F.
20
40
60
80
100
120
140
160
TIME OF RESTING - Hours

FIGURE 12

When the final concentration of pigment is small and masterbatch is used for convenience the problem is simple and many such masterbatches are already available. The preferred method for their preparation is high viscosity milling, i.e., in a stiff plastic paste. This technique--at least for carbon black--was borrowed from the rubber industry. In rubber technology the reinforcing effect of carbon black was discovered first. When the importance of good dispersion was appreciated, high viscosity milling became accepted procedure.

For plastics the stiff-mix milling method has already been accepted. The next step would seem to be a study of the reinforcing effect of carbon black and other finely divided pigments. Every man-made article can be improved and some day will be. Many synthetic resins and plastics seem to form with carbon black a carbon-to-polymer bond. High loadings become insoluble just as they do in rubber when the carbon gel complex becomes coextensive with the whole mix. One can reasonably predict that a systematic study of pigment-plastic systems covering variables such as, pigment fineness, pigment morphology, pigment surface chemistry, dispersing agents, bonding agents and volume concentration will result in new products as different as stationers' rubber bands are from passenger tire treads. As a contribution to this end, carbon black can offer more combinations of fineness, morphology and surface chemistry than any other pigment.

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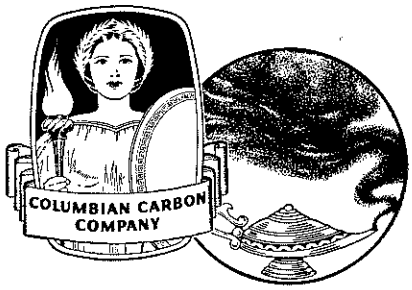
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